1 Total Aroclors in Area 1 Formerly Impounded Sediments

Total Aroclor concentrations from the 2017 and 2018 pre-design investigation (PDI) samples collected by Wood Environment & Infrastructure Solutions, Inc. on behalf of Georgia-Pacific in the formerly impounded floodplains of OU5/Area 1were unexpectedly lower than total Aroclor concentrations in samples collected from this same area in 2008, 2001 and 1993/1994 by USEPA, MDEQ and Georgia-Pacific. Pre-2017 data for this Area have consistently shown that low lying areas (e.g., old river channels and low flat terraces) have total Aroclor concentrations averaging approximately 10 mg/kg or more. These same data also commonly exceeded total Aroclor concentrations of 20 mg/kg, with occasional exceedances of 50 mg/kg (i.e., TSCA material). The Aroclor concentrations in the pre-2017 data are spatially heterogeneous, but with some predictable trends including thicker sediment deposits with higher concentrations within old thalwegs. Temporal trends over the last 30 years in these Aroclor concentrations are not expected because concentrations are generally lower than those for which substantive bio-degradation might be occurring, the PCBs are bound with highly organic recycled paper residuals, and PCBs have been shown to be environmentally persistent organic pollutants (POPS).

Contrary to this understanding of fate and transport of Aroclors in OU5/Area 1, the total Aroclor concentrations in PDI samples (collected in 2017 and 2018)are distinctly lower than those in the RI/FS data (collected from 1993 through 2008) (Figure 1 Figure 2). In an effort to understand this data inconsistency, a series of investigations was conducted, and are identified below:

1) Understanding of temporal changes in total Aroclors in floodplain soils was based on statistical analyses conducted by Kern 2001. These analyses indicated no differences in total Aroclor distributions between 1993/1994 and 2001. These analyses were reviewed and key graphics reproduced in this report.
2) It was suggested that preferential sectioning of cores based on stratigraphy (e.g., focused collection of sediment layers exhibiting visual clues for contamination) could explain apparent bias between PDI and RI/FS data. Consequently, a comparison of total Aroclors was conducted for cores that were a.) in close proximity (i.e., 15 feet) of each other and b.) were sectioned consistently. This comparison was to determine if there were differences in total Aroclors that could not be explained by these differences in segmenting the cores or core handling procedures.
3) Differences in laboratory analytical methods were evaluated by comparing split samples sent to the PDI lab used by Georgia Pacific and an alternative laboratory used by MDEQ.
    a. Standard certified reference material (CRM) prepared by Environmental Resource Associates (ERA) was also sent to the MDEQ laboratory to evaluate accuracy of reported Aroclors in the MDEQ split samples.

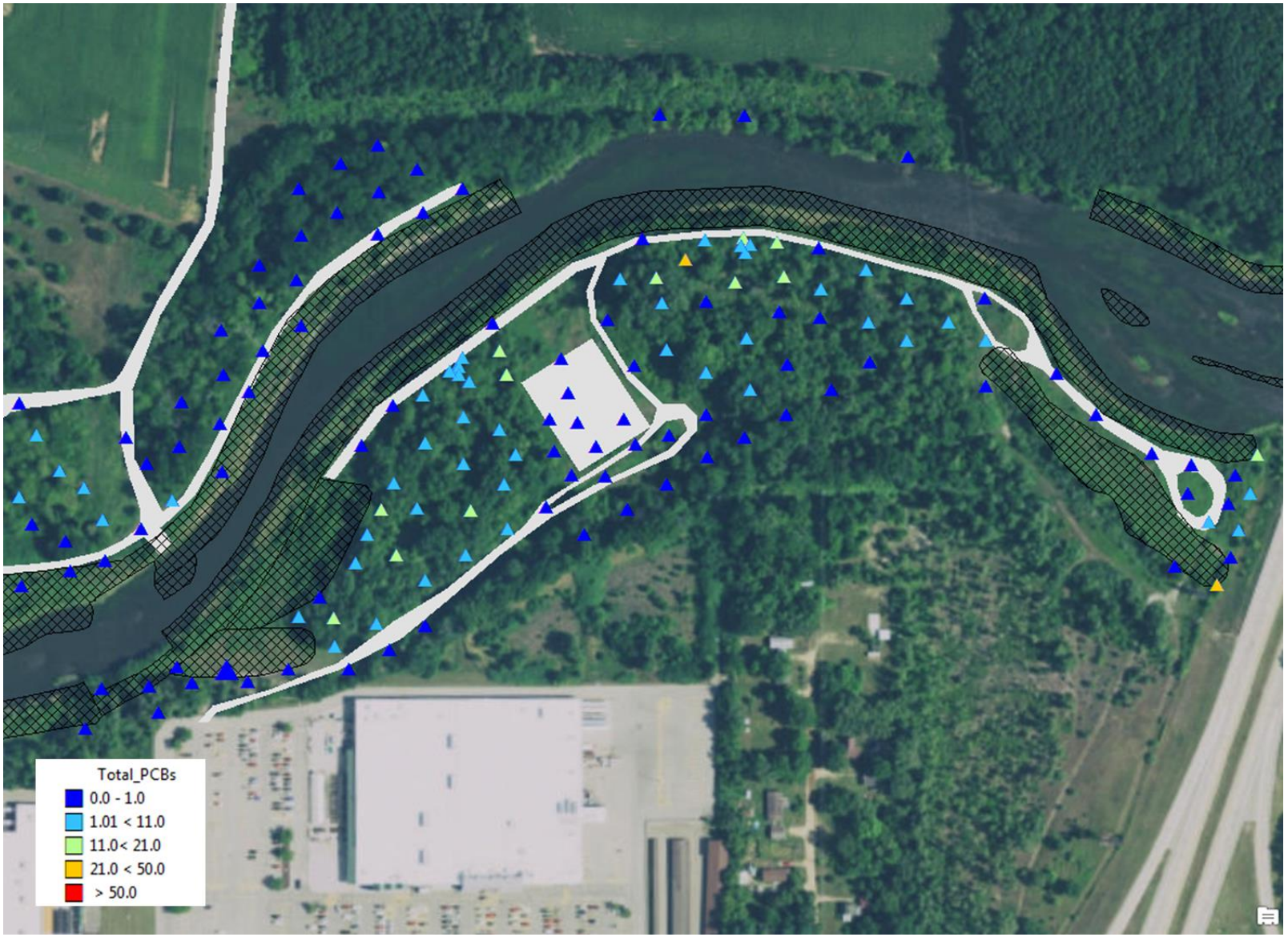


Figure 1. Total Aroclor concentrations in 0 to 6 inch depth interval for samples collected in 2017 and 2018 pre-design investigation.

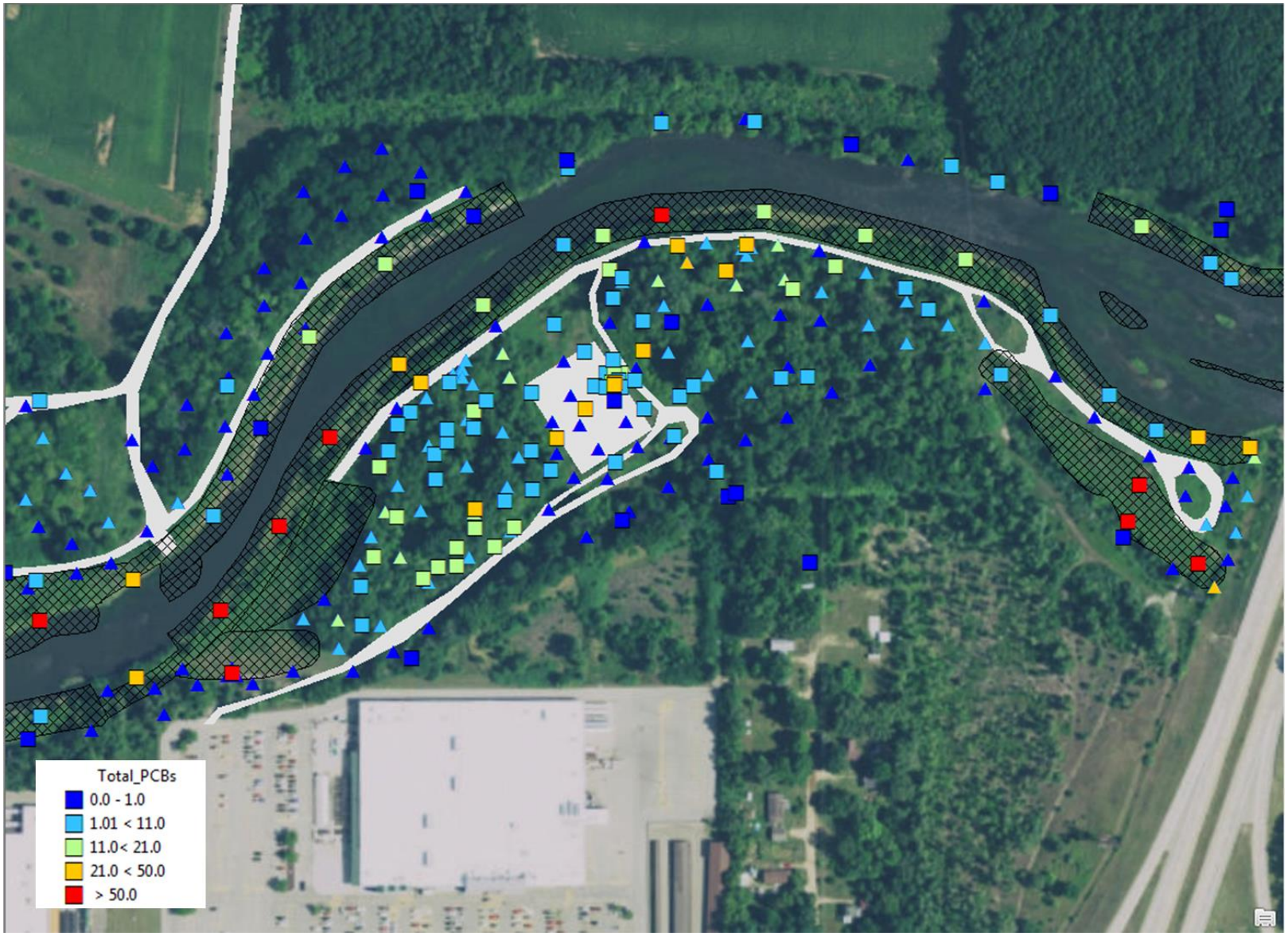
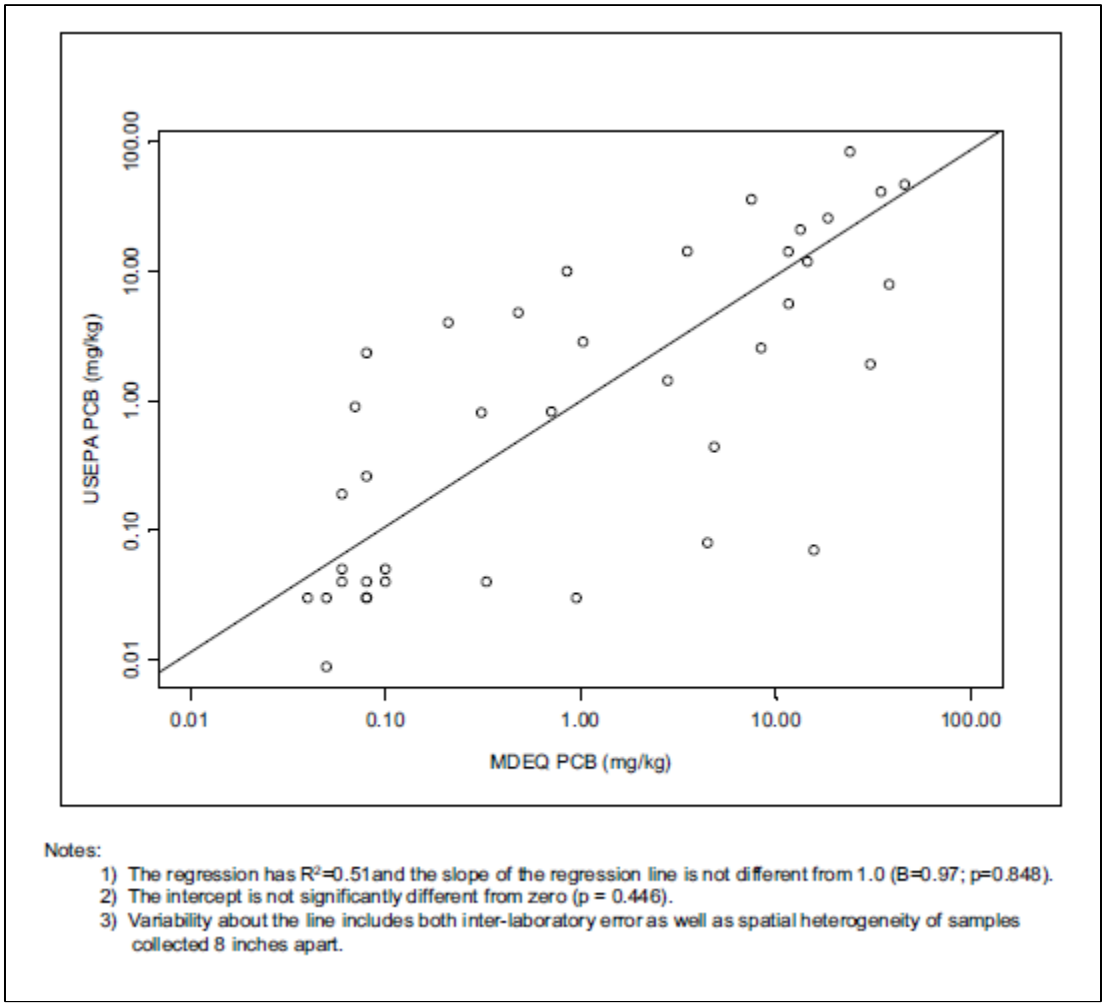


Figure 2. Total Aroclor concentrations in 0 to 6 inch depth interval for samples collected in 2017 and 2018 pre-design investigation (triangles) and in RI/FS investigations (squares)

1.1 Temporal Trends from 1993 to 2001

Kern (2001) conducted an analysis comparing PCB Aroclor samples collected in 1993 with samples collected in 2001. The 1993 data were collected by the Blasland Bouck and Lee (BBL) on behalf of Georgia Pacific, and the 2001 data were collected by Weston Solutions on behalf of the United States Environmental Protection Agency, with limited split samples collected by the Michigan Department of Environmental Quality also in 2001. These data were subjected to careful data handling and statistical analyses by Kern Statistical Services to evaluate potential temporal trends in total Aroclors in exposed formerly impounded sediments and instream sediments at Plainwell and Otsego City Impoundments. Kern (2001) found that the median and statistical distributions of formerly impounded and instream sediments were not statistically different, and that total Aroclors from split samples collected by the MDEQ and USEPA were variable, but exhibited little or no bias. As can be seen from the following figure split samples are evenly spread around a regression line with slope 0.97 which is nearly identical to the 1:1 line, representing unbiased measures.



Notes:
1) The regression has R^2=0.51and the slope of the regression line is not different from 1.0 (B=0.97; p=0.848).
2) The intercept is not significantly different from zero (p = 0.446).
3) Variability about the line includes both inter-laboratory error as well as spatial heterogeneity of samples collected 8 inches apart.

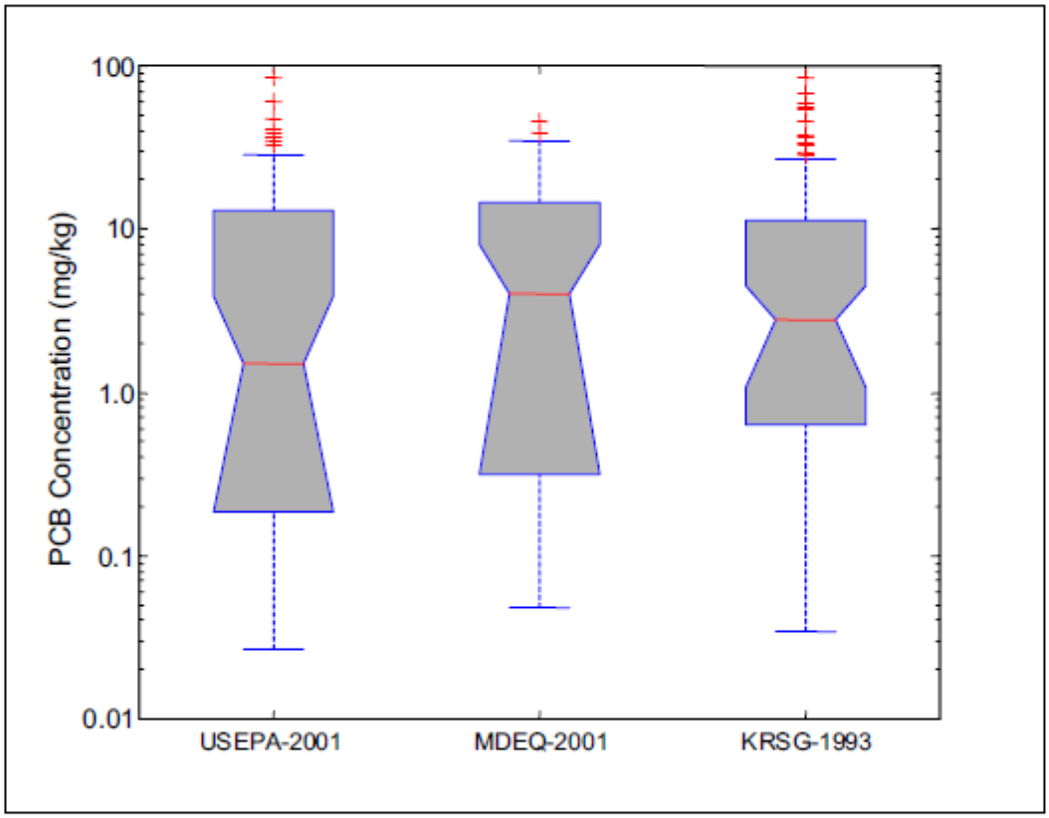
Figure 3. USEPA total Aroclors vs MDEQ total Aroclors collected in 2001 from Plainwell Impoundment and Otsego City Impoundments (Reproduced from Kern, 2001).

The distribution of formerly impounded sediments from these three sets of samples are displayed as side by side boxplots in **Figure *4***. This figure shows that the 25th and 75th percentiles (top and bottom of gray boxes) are nearly identical and that confidence intervals (notches in boxes) median total Aroclor concentrations (red horizontal line) are strongly overlapping. Statistical tests performed in 2001 indicate these median concentrations do not differ statistically (Kruskall Wallace; p= 0.41). In the Kern report this comparison was reported as evidence of comparability because there was general agreement that there would be no trends in total PCBs in floodplain soils because PCBs are persistent pollutants and do not generally degrade perceptibly even over very long periods of time.

FIGURE 4.

ALLIED PAPER, INC./PORTAGE CREEK/KALAMAZOO RIVER SUPERFUND SITE
USEPA REMOVAL ASSESSMENT STAGE I DATA EVALUATION

BOX PLOTS OF PCB CONCENTRATION IN TOP TWO FEET
OF EXPOSED SEDIMENTS AT PLAINWELL IMPOUNDMENT



Notes:
1) The ends of each box represent the 25th and 75th percentiles (quartiles).
2) The "notches" represent approximate 95% confidence intervals for the median.
3) The length of each whisker is 1.5 times the inter-quartile range (IQR).
4) Plus symbols represent values greater than 1.5 times the IQR from the median.

Figure 4. Comparison of 1993 and 2001 total Aroclors reported by Kern Statistical Services (2001).

1.2 Aroclors in Similarly Sectioned Proximal Core Samples

Core samples from the RI/FS were paired spatially with PDI cores within 15 feet and 20 feet. These pairs were examined to identify instances where core sections in both locations were sectioned regularly into 0 to 6, 6 to 12, 12 to 24 inch intervals. This pairing of core sections for which both cores were sectioned

identically provided a control for any bias related to preferential sectioning of cores in the RI/FS data. These paired core sections were plotted in three ways:

1) Total Aroclors in the PDI samples were plotted against total Aroclors in the RI/FS samples and 1 to 1, 2 to 1, 10 to 1 and 100 to 1 lines were overlaid on the plots (Figure 5). Equivalent analyses would be indicated by an equal scatter of sample pairs above or below the 1 to 1 line.
2) Ratios of the RI/FS samples divided by PDI samples were plotted:
    a. Against distance between pairs
    b. Against concentration in the RI/FS samples

1.2.1 PDI vs RI/FS Paired Core Sections

Paired PDI and RI/FS total Aroclors are plotted in Figure 5 showing that for pairs of cores sectioned identically and within 15 feet of each other resulted in substantively lower Aroclor concentrations in PDI core sections as compared with RI/FS cores. For these paired core sections, all but one resulted in the RI/FS sample having higher concentrations than the PDI samples. The RI samples were generally on the order of a factor of 2 higher than the PDI samples with some instances where the RI/FS total Aroclors were a factor of 10 higher or more. This systematic bias between the sampling and analysis programs confirms the apparent differences in maps of RI/FS vs PDI sample results. Further it is notable that factor of 2 differences are observed at both the low and high end of the concentration range. Particularly important are factor of 2 or greater ratios for samples of 10 mg/kg and 20 mg/kg which can be expected to influence estimates of exposure in areas with concentrations close to the remedial action limits (RAL).

1.2.2 Ratio of PDI to RI/FS total Aroclors

The ratio of total Aroclor concentration in RI/FS samples to PDI samples are plotted against distance between core location in (Figure 6). The ratios are greatest for sample pairs within approximately 15 feet with values ranging from just over 1 to 1 to as much as 50 to 1. The ratios are more or less randomly distributed for distances greater than about 15 feet which is expected regardless of the degree of agreement between sample values because spatial heterogeneity in the concentrations is expected to cause paired values to be independent and therefore the ratios should be randomly distributed about the value of 1.0.

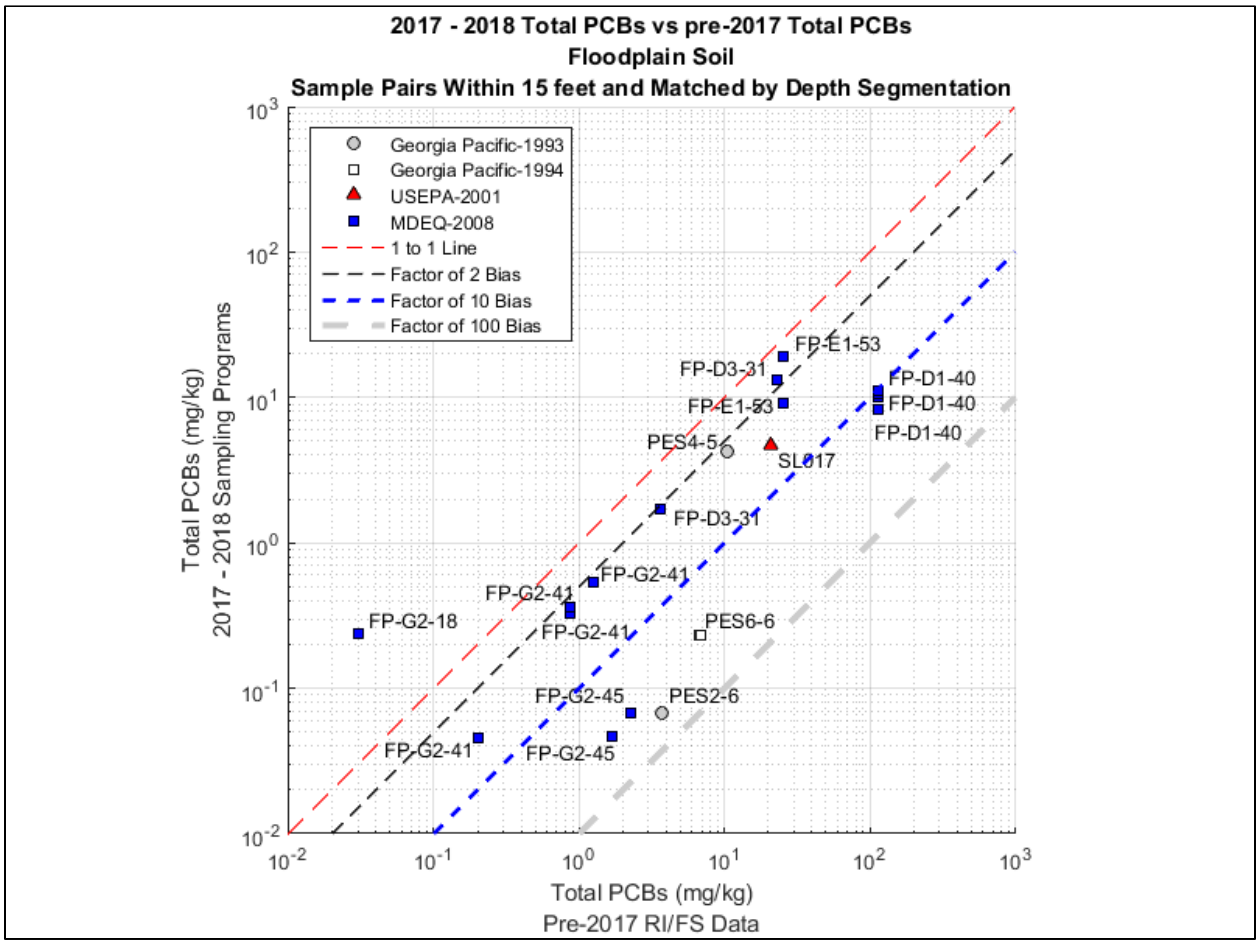


Figure 5. Total Aroclors in PDI samples vs total Aroclors in RI/FS samples for cores sectioned identically and within 15 feet in proximity.

The ratios of PDI to RI-FS samples are also plotted against total Aroclors in the RI/FS samples showing that the ratio generally increases with concentration in the RI samples, and that for RI samples with total Aroclors exceeding 15 mg/kg all ratios are greater than 1 with most ratios greater than 2 and with several ratios exceeding 10 (Figure 7). This indicates that at locations sampled in 2017 and 2018 and forming the basis for mapping total Aroclors and determining exposure, mapped values may differ from maps developed for the RI/FS by a factor of 2 or more.

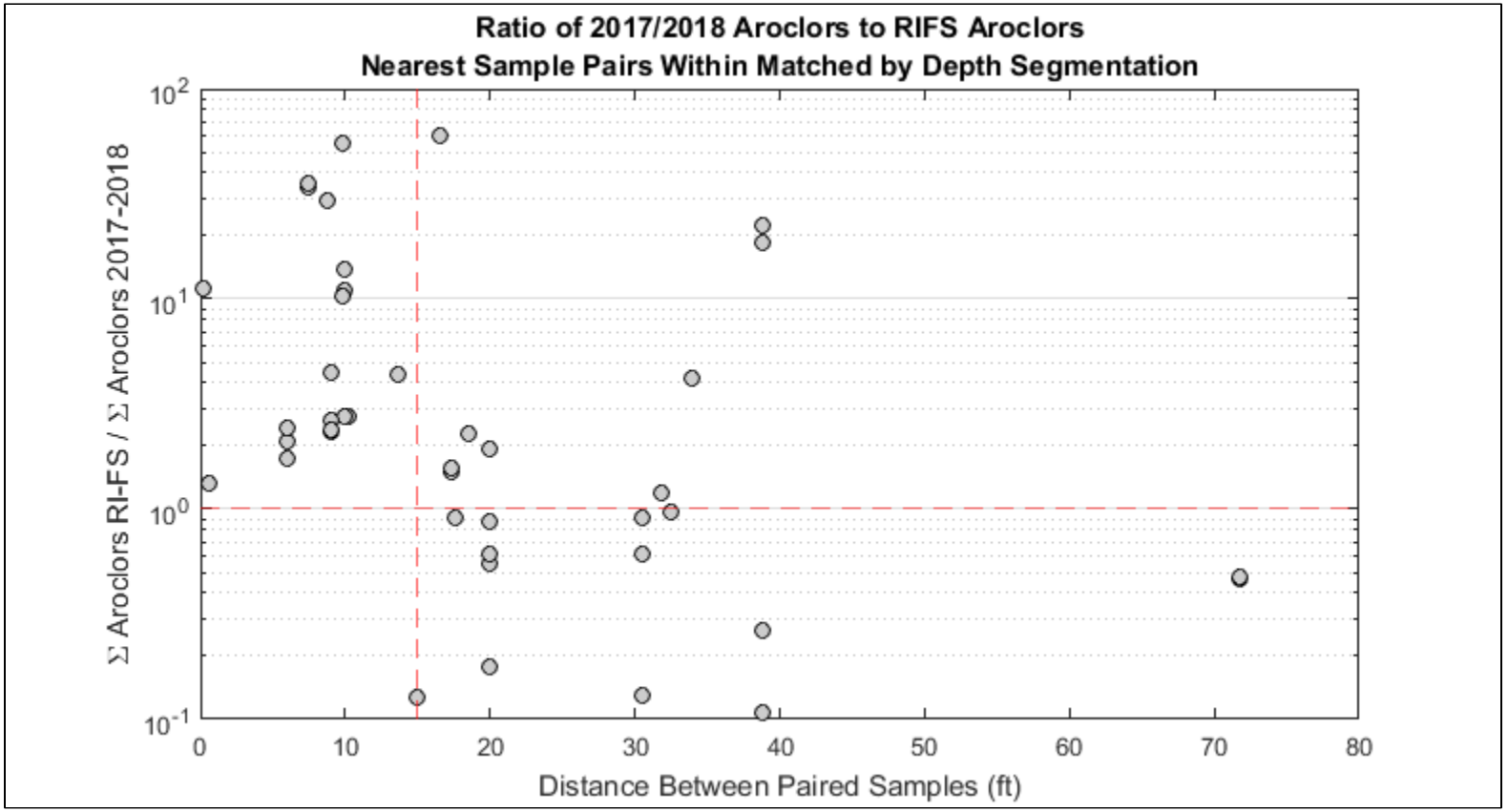


Figure 6. Ratio of PDI to RI/FS total Aroclors against distance between core locations.

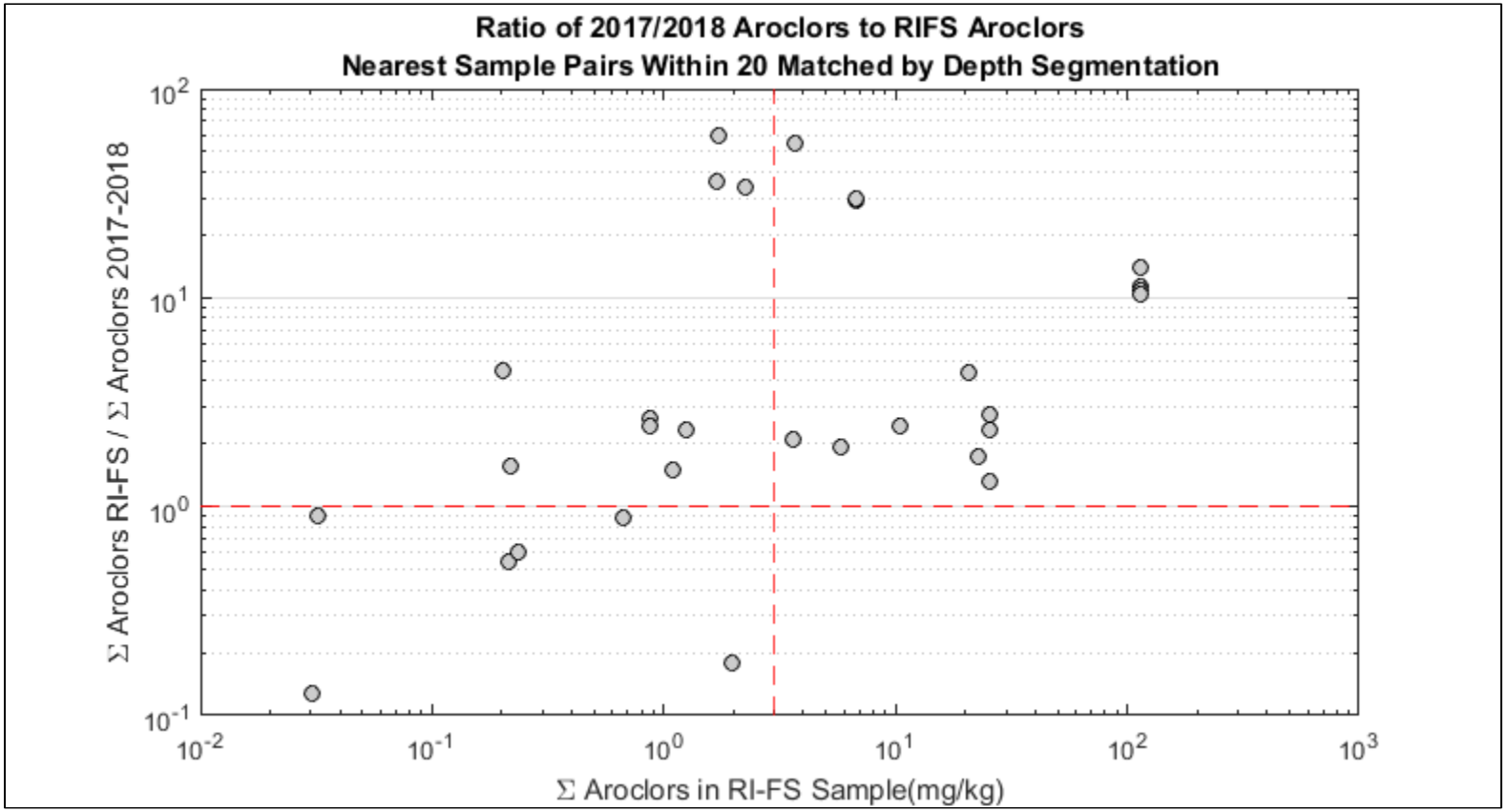


Figure 7. Ratio of PDI to RI/FS total Aroclors against total Aroclor concentratoin in RI-FS sample.

1.3 Laboratory Split Samples

Twenty-two samples were spit and analyzed by both MDEQ and Wood to test for inter-laboratory differences in total Aroclor quantitation. The MDEQ laboratory reported more Aroclors (Aroclors 1262 and 1268) contributing to the totals than the Wood laboratory, so total Aroclors were compared in two ways; first based on total of all Aroclors reported by each laboratory and secondly based only on the total of Aroclors reported by the Wood laboratory. Some statistical results were sensitive to this data handling choice.

When considering the full set of Aroclors, values reported by MDEQ exceeded those reported by Wood in 15 of 20 pairs, whereas when restricting the MDEQ totals to only those Aroclors reported by Wood, the MDEQ totals exceeded the Wood totals in 13 of 20 cases. On average, for all Aroclors, the ratio of MDEQ to Wood total Aroclors was R=1.5 (CI: 1.4, 1.6). For the restricted set of Aroclors reported by Wood, the ratio was R=1.4 (CI: 1.1, 1.7). Because the lower confidence limits are greater than 1.0, one can conclude that total Aroclor concentrations reported by Wood are less than those reported by MDEQ by approximately a factor of 1.5 (1.4 for restricted set of Aroclors) with 95% level of confidence. These analyses are presented in Figure 8 and on Table 1.

The pairs were also subjected to nonparametric sign test which tests the null hypothesis that the median concentrations of each set of data are equal, based on a paired statistical design. For the full set of Aroclors, the sign test indicated differences in medians at the 95% level of confidence, whereas for the reduced set of Aroclors, median total Aroclors were not found to differ.

Summarizing, these results are not fully consistent, although for three of four evaluations (Ratios, full and reduced Aroclor set, and sign test full set of Aroclors) the tests indicated statistical differences and on average the total Aroclors reported by Wood were on the order of 50% lower than those reported by MDEQ for the full and reduced set of Aroclors.

Michigan DEQ also submitted a CRM performance standard to the analytical lab and found that the reported value was on the low end of ERA's QC performance acceptance limits (QC-PAL), which suggests that the low bias identified in split samples is indicative of inaccuracy in the laboratory results reported by Wood. Table 2 contains a summary of MDEQ's CRM sample recoveries as compared to ERA's QC-PAL, mean reported result and true value of the associated Aroclor.

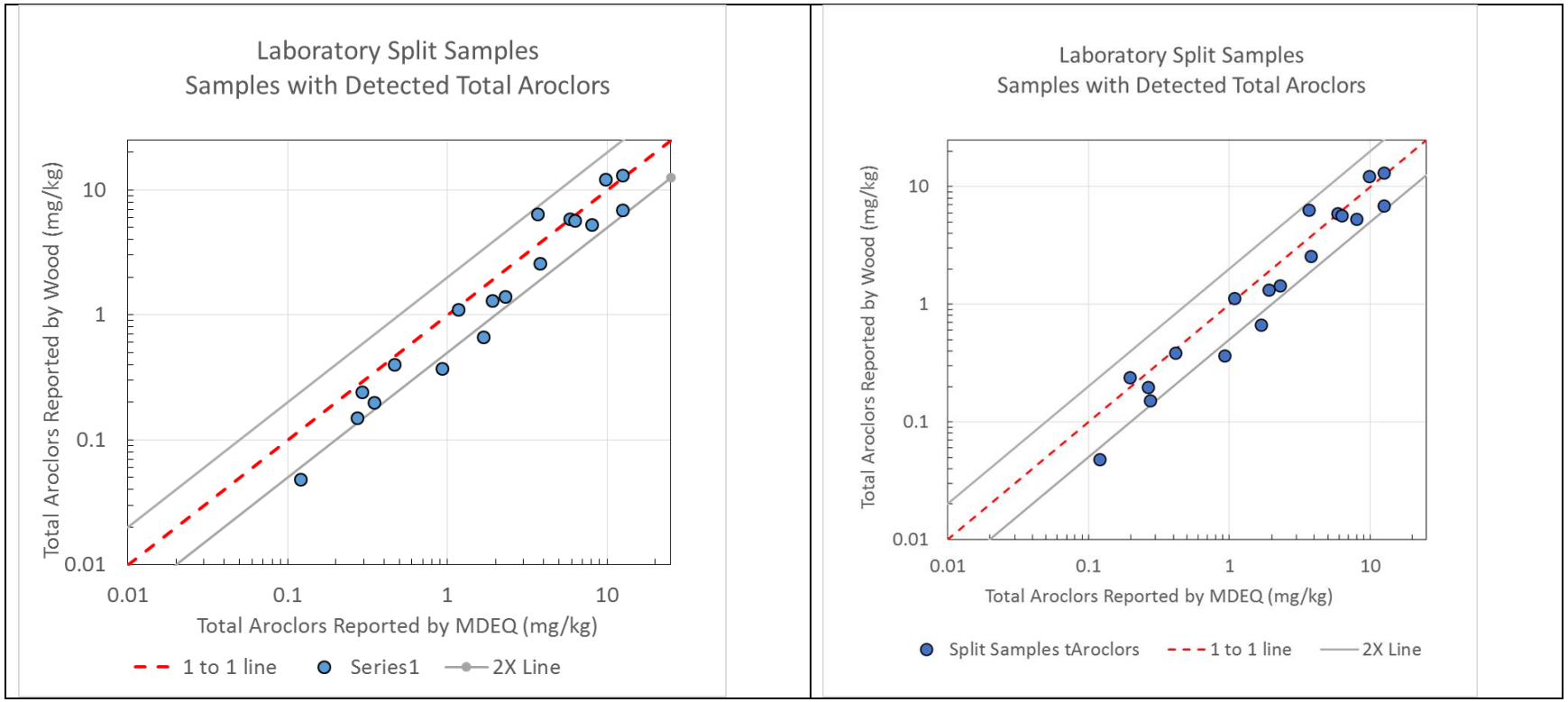


Figure 8. Total Aroclors reported by Wood vs reported by MDEQ in split samples for the full set of Aroclors (left panel) and for the restricted set of Aroclors (right panel).

Table 1. Split sample total Aroclor results for Plainwell Impoundment floodplain soils.								
			Total Aroclors MDEQ (mg/kg)		Total Aroclors Wood (mg/kg)			
sys_loc_code	Start Depth	End Depth	Full Aroclor Set	Reduced Aroclor Set	Reduced Aroclor Set	Ratio (Full) (MDEQ/Wood)	Ratio (Reduced) (MDEQ/Wood)	DEQ > Wood?
A1-FPS-142	0	6	5.86	5.86	5.89	0.99	0.99	0
A1-FPS-144	6	12	0.292	0.197	0.24	1.22	0.82	0 (1)
A1-FPS-146	12	24	6.29	6.29	5.72	1.10	1.10	1
A1-FPS-153	6	12	0.349	0.264	0.198	1.76	1.33	1
A1-FPS-178	12	24	0.014	<0.011	<0.042		No Estimate	
A1-FPS-183	0	6	0.713	0.606	<0.042		No Estimate	1
A1-FPS-183	12	24	1.9	1.895	1.32	1.44	1.44	1
A1-FPS-188	6	12	<0.011	<0.011	<0.042		No Estimate	
A1-FPS-196	6	12	<0.009	<0.009	0.06		No Estimate	0
A1-FPS-201	6	12	0.12	0.12	0.048	2.50	2.50	1
A1-FPS-206	6	12	1.17	1.09	1.12	1.04	0.97	0(1)
A1-FPS-213	6	12	3.65	3.65	6.35	0.57	0.57	0
A1-FPS-217	0	6	12.5	12.46	13.2	0.95	0.94	0
A1-FPS-236	12	24	0.273	0.273	0.152	1.80	1.80	1
A1-FPS-246	6	12	0.465	0.414	0.389	1.20	1.06	1
A1-FPS-256	0	6	9.81	9.809	12.2	0.80	0.80	0
A1-FPS-281	12	24	1.68	1.677	0.67	2.51	2.50	1
A1-FPS-304	6	12	0.926	0.926	0.364	2.54	2.54	1
A1-FPS-312	0	6	3.78	3.781	2.56	1.48	1.48	1
A1-FPS-316	0	6	8.02	8.02	5.33	1.50	1.50	1
A1-FPS-338	0	6	2.29	2.292	1.44	1.59	1.59	1
A1-FPS-351	6	12	12.5	12.53	6.9	1.81	1.82	1

Table 2 MDEQ Summary of Recoveries of Certified Reference Material

Sample #:		CRM PCB IN SOIL 1248-496				CRM PCB IN SOIL 1260-494				CRM PCB IN SOIL 1254-492			
Field ID:													
Lab ID:		05171-025				05171-026				05171-027			
Date Sampled:		06/27/2018				06/27/2018				06/27/2018			
Depth(ft):		True Value =		4.91	Mean	True Value =		3.19	Mean	True Value =		3.31	Mean
	CAS	QC Range (n=66)		2.24 - 6.19	2.98	QC Range (n=62)		1.38 - 3.73	2.59	QC Range (n=67)		1.36 - 4.04	2.65
PCB's (mg/Kg)		Conc	Q	RL	MDL	Conc	Q	RL	MDL	Conc	Q	RL	MDL
Aroclor-1016	12674-11-2	ND		0.00168	0.000672	ND		0.00168	0.000672	ND		0.00167	0.000668
Aroclor-1221	11104-28-2	ND		0.00168	0.000672	ND		0.00168	0.000672	ND		0.00167	0.000668
Aroclor-1232	11141-16-5	ND		0.00168	0.000672	ND		0.00168	0.000672	ND		0.00167	0.000668
Aroclor-1242	53469-21-9	ND		0.00168	0.000672	ND		0.00168	0.000672	ND		0.00167	0.000668
Aroclor-1248	12672-29-6	2.29	D	0.017	0.00673	ND		0.00168	0.000672	ND		0.00167	0.000668
Aroclor-1254	11097-69-1	ND		0.00168	0.000672	ND		0.00168	0.000672	2.22	D	0.033	0.013
Aroclor-1260	11096-82-5	ND		0.00168	0.000672	1.86	D	0.017	0.0067	ND		0.00167	0.000668
Aroclor-1262	37324-23-5	ND		0.00168	0.000672	ND		0.00168	0.000672	ND		0.00167	0.000668
Aroclor-1268	11100-14-4	ND		0.00168	0.000672	ND		0.00168	0.000672	ND		0.00167	0.000668
Total	1336-36-3	**2.29**	D	0.017	0.00673	**1.86**	D	0.017	0.0067	**2.22**	D	0.033	0.013
		76.85% %		Recovery from mean		71.81% %		Recovery from mean		83.77% %		Recovery from mean	
		46.64% %		Recovery from true value		58.31% %		Recovery from true value		67.07% %		Recovery from true value	
				Recovery of mean	60.60%			Recovery of mean	81.30%			Recovery of mean	80.10%

ND – nondected Q – lab qualifier RL – reporting limit MDL – method detection limit

D – result from diluted sample analysis